

PATENT SPECIFICATION

1,106,708

DRAWINGS ATTACHED.

1,106,708



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COMPLETE SPECIFICATION.

Improvements in or relating to Electrodes for Fuel Cells.

We, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION, an Australian body corporate established under the Science and Industry Research Act, 1949, of 314 Albert Street, East Melbourne, in the State of Victoria, Commonwealth of Australia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

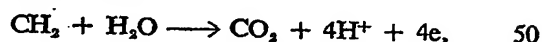
This invention relates to improvements in catalysts for the electrochemical oxidation of organic compounds. The electrochemical oxidation of organic compounds is currently of considerable interest in connection with the possible use of cheap fuels in fuel cells. It is desirable in such applications to obtain complete oxidation of the organic fuel to water and carbon dioxide and the general object of this invention is to provide new catalysts which are superior to those currently used.

Early workers in this field have shown that pure platinum is a catalyst for the electrochemical oxidation of water-soluble organic compounds such as methanol, formaldehyde, and formic acids. More recently it has been shown that platinum is also a catalyst for water-insoluble organic materials such as diesel oil, propane, and many other hydrocarbons.

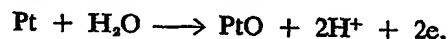
It has now been found that the major loss in efficiency of a platinum catalyst occurs through the progressive poisoning of the surface by intermediate products. This effect is apparent in the oxidation of water-soluble organic materials up to temperatures of at least 80°C and probably extends up to 150–200°C, at which temperatures hydrocarbon oxidations are currently being carried out.

A proposed mechanism for the electro-

chemical oxidation of formaldehyde to carbon dioxide in an acid electrolyte (Koch.:Proc. of the first Australian Conference on Electrochemistry, Jan. 1963) suggests that the overall reaction involving four electrons,



may occur in stages of single electron transfer. The intermediate oxidation products which are absorbed on the surface may react with each other to produce a less reactive species which poisons the surface. This type of mechanism also applies in the oxidation of acetylene (Wroblowa et al. J. Electroanal. Chem. 6, 401, 1963). It has also been shown that when the potential of a platinum surface reaches the value at which oxygen can be chemisorbed (i.e. more anodic than +0.6v. versus a normal hydrogen electrode, N.H.E.) the poisoning agent is removed. We have also found that the formation of a poison is hindered at potentials more positive than +0.6v. The oxygen on the platinum surface possibly arises from a reaction of the type:—



where the aqueous electrolyte provides the required water molecule.

The potential (+0.6v.) at which oxygen can be chemisorbed on platinum is far more anodic than the thermodynamic potential for formaldehyde oxidation to carbon dioxide (–0.07v.). Most organic fuels will have potentials near 0.0v. vs. N.H.E. so that there is a considerable loss in efficiency when platinum is used as a catalyst.

(The efficiency of a fuel cell may be expressed as the ratio between the working

cell voltage and the thermodynamic reversible voltage E_R , i.e.

$$\text{efficiency (\%)} = \frac{V}{E_R} \times 100.$$

For a formaldehyde-oxygen cell $E_R = 1.30\text{v.}$ and if the fuel electrode is at $+0.6\text{v.}$ and the oxygen-electrode $+0.8\text{v.}$ (these figures are practical ones for a membrane-type fuel cell at a current density of 20 mA/cm^2) the efficiency is only 15.4% . At least a 40% efficiency is desirable in a fuel cell).

Published work therefore indicates the desirability of chemisorbed oxygen on the catalyst surface.

This invention therefore seeks to provide a catalyst for the electrochemical oxidation of an organic fuel capable of performing two vital functions, i.e.

- (a) It must absorb the organic molecule and facilitate electron transfer from it.
- (b) There must be oxygen chemisorbed on to the catalyst in the region of 0.0v. (vs. N.H.E.) to prevent poisoning of the surface by intermediate products of oxidation.

We have now found that by combining elements with property (a) with those of property (b) a catalyst can be produced which is very much more active than one having property (a) alone.

Accordingly, in its broadest aspect, the present invention provides an electrode for a fuel cell comprising a conducting substrate having deposited thereon a catalyst which comprises an alloy (as hereinafter defined) consisting of or comprising (i) a metal which is capable of absorbing an organic molecule and facilitating electron transfer from the molecule, and (ii) at least one other metal which at a potential of about 0.0v. versus a normal hydrogen electrode is capable of chemisorbing oxygen and selected from the group comprising Pb, Tl, Sn, As, Sb, Bi, and Re, said alloy being produced by co-deposition from solution.

Property (a) is present in the transition metals (Group VIII of the Periodic Table) such as Ni, Pt, Pd, Rh, Ir, Os and other such metals already known to have catalytic activity in connection with fuel cells. Property (b) is not directly known for most metals but a guide to the tendency to chemisorb oxygen may be obtained by calculating the standard potential of formation of the oxides. Pb, Tl, Sn, As, Sb, Bi, Re, are elements showing standard potential of oxide formation nearer 0.0v. than platinum, and their choice would depend partly on the stability of the oxide in the electrolyte.

For convenience of expression the terms "alloy" and "alloy as hereinbefore defined"

are used throughout this specification to signify a composition containing two or more metals in intimate admixture and are to be understood to include compositions in which the metallic constituents do not form a true alloy in the usually accepted sense. For example it is well known that pure rhenium metal is electrodeposited from aqueous solution only at potentials more negative than the reversible hydrogen potential and that hydrogen accompanies its deposition. In the present case, in which co-deposition takes place from a solution of two or more metal ions, rhenium metal may deposit as an alloy with platinum, but also a mixture of a low valence rhenium oxide with platinum is likely to be deposited at potentials more positive than the reversible hydrogen potential. Other metals may also behave in this manner, and we therefore do not intend to limit ourselves to catalysts consisting only of metals per se.

More specifically, therefore, the invention provides a fuel cell electrode in which the catalyst comprises an alloy (as hereinbefore defined) consisting of or comprising (i) a metal selected from the transition elements, and (ii) at least one other metal selected from the group comprising Pb, Tl, Sn, As, Sb, Bi, and Re having a calculated standard potential of oxide formation between 0.0v. and that of platinum, said alloy being produced by co-deposition from solution.

Preferably the transition metal (i) is selected from the group comprising Ni, Pt, Pd, Rh, Ir, Os. It is also preferred that the alloys are produced by electrochemical deposition from solutions containing the metals concerned.

The invention thus also includes a method of producing an electrode which comprises co-depositing on a conducting substrate an alloy (as hereinbefore defined) of a metal of type (i) above and at least one other metal as defined above of type (ii) from a solution containing the metals by means of chemical or electrochemical reduction.

The invention further includes a fuel cell in which an organic material is oxidised electrochemically at an electrode of the type described.

In a fuel cell employing an organic fuel, it is desirable to use an acid electrolyte because the resulting carbon dioxide can be readily removed as a gas and, in this case therefore, the choice of a catalyst is restricted to a metal of type (i) together with a metal of type (ii) which is stable in an acid medium in the presence of chemisorbed oxygen. Any of the metals Pt, Pd, Rh, Ir, Os, all of type (i) would be stable in acid but Re is the only one of type (ii) which we have found to provide a stable catalyst. Although alloys of Pb, or Tl with platinum are effective catalysts, their life in

an acid electrolyte is limited by either dissolution or the formation of an insoluble salt (e.g. PbSO_4). If used in an alkaline medium the life of these catalysts may be considerably extended.

The following examples illustrate the principles and techniques of the invention:

EXAMPLE I.

Binary alloys of platinum (Pt) with Pb, Ti, Sn, As, Sb, Bi, Pd, Hg, Re and Mo were prepared by electrochemical deposition from mixed solutions on a platinum substrate. Typical examples of the plating procedures are as follows:—

Alloy	Pt/Re	Pt/Pb
Plating Solution Composition	1% Pt as H_2PtCl_6 0.65% Re as KReO_4 pH3 in excess NaCl	1% Pt as H_2PtCl_6 0.6% Pb as Pb(OAc)_2 in 1M HCl
Deposition Potential (vs. NHE)	+0.05v.	+0.05v.

The correlation obtained between the potential of oxide formation and activity as catalysts in the electrochemical oxidation of formaldehyde for pure platinum and the above binary alloys are shown in the accompanying drawing, in which, E_0 is the calculated standard potential of oxide formation which, in all cases other than pure platinum refers to the element which is alloyed with platinum, in the catalyst; and $\log i$ is the logarithm of the experimental anodic current density (mA per sq. cm.) in formaldehyde at +0.5v. The data refers to a single electrode. For use in a fuel cell this single electrode would have to be coupled with an oxygen cell. However, as

the behaviour of the oxygen electrode in most cases is independent of the fuel electrode, any improvement in the fuel electrode will reflect an improvement in the complete fuel cell (this is shown in Example II).

EXAMPLE II.

A Pt/Re deposit of the type described in Example I was applied to a platinum-impregnated membrane as described in British Patent Specification No. 1,013,703, and incorporated in a formaldehyde-oxygen membrane-type fuel cell. The working parameters of the cell are compared in Table I with those of a cell using a membrane impregnated with pure platinum:

TABLE I

Current Density (mA/cm ²)	Pt	Cell Voltage	Pt/Re
Nil	0.73		0.93
10	0.35		0.62
20	0.30		0.50

The calculated efficiencies of the two fuel cells at a current density of 20 mA/cm² are 23 and 38 per cent respectively for Pt and Pt/Re-impregnated membranes.

EXAMPLE III.

Catalysts comprising ternary alloys of platinum have been found to be very active catalysts and good results have been obtained with a platinum/rhenium/tin catalyst deposited from a plating solution containing 0.5% Pt, (as H_2PtCl_6) 1% KReO_4 , 0.075% Sn, deposited at a potential of +0.05v. vs. N.H.E. with a loading of about 3 mg. Pt and 0.5 mg. Re per cm². Com-

parable activities were obtained with deposits on substrates of platinum, tantalum, gold or stainless steel 316 as quoted in Lange's Handbook of Chemistry (8th Edition) Page 841.

A life test of a deposit of the above type on platinum in a solution containing 2M HCHO and 1N H_2SO_4 at 60°C showed a potential of +0.2v. after 1000 hours operation at 100mA/cm².

A catalyst of this type is also active in the oxidation of a wide range of organic compounds. Typical results are given in Table II.

TABLE II
Current Density at
+0.3v. vs. N.H.E.
(mA/cm²)

	Compounds (Concentration)		Temperature (°C)
5	Formic Acid (IM)	100	60
	Formaldehyde (IM)	300	60
	Methanol (IM)	10	60
	Methanol (IM)	50	85
	Eethanol (IM)	40	83
10	Ethylene Glycol (IM)	10	84
	Glycerol (IM)	8	84
	Sucrose (O.IM)	0.9	84

The reaction rates for the cell reactions (and hence the maximum current density attainable) can sometimes be further increased by raising the pH of the electrolyte, e.g. by using 0.1N H₂SO₄, the total ionic concentration being maintained by the addition of a neutral electrolyte, for example, lithium sulphate.

WHAT WE CLAIM IS:—

1. An electrode for a fuel cell comprising a conducting substrate having deposited thereon a catalyst which comprises an alloy (as hereinbefore defined) consisting of (i) a metal which is capable of absorbing an organic molecule and facilitating electron transfer from the molecule and (ii) at least one other metal which at a potential of about 0.0v versus a normal hydrogen electrode, is capable of chemisorbing oxygen, and is selected from the group comprising Pb, Tl, Sn, As, Sb, Bi, and Re said alloy being produced by co-deposition from solution.

2. An electrode as claimed in Claim 1 wherein the metal (i) is selected from Group VIII of the Periodic Table.

3. An electrode as claimed in Claim 2 wherein the metal (i) is selected from the group comprising Ni, Pt, Pd, Rh, Ir and Os.

4. An electrode for a fuel cell comprising a conducting substrate having deposited thereon a catalyst comprising an alloy (as hereinbefore defined) of platinum and rhenium, said alloy being produced by co-deposition from solution.

5. An electrode as claimed in Claim 4 wherein the alloy also contains tin.

6. A method for producing an electrode for a fuel cell which comprises the steps of co-depositing on a conducting substrate by means of chemical or electrochemical reduction from solution an alloy (as hereinbefore defined) of (i) a metal which is capable of absorbing an organic molecule and facilitating electron transfer from the molecule and (ii) at least one other metal

which, at a potential of about 0.0v. versus a normal hydrogen electrode, is capable of chemisorbing oxygen, and is selected from the group comprising Pb, Tl, Sn, As, Sb, Bi, and Re.

7. A method as claimed in Claim 6 wherein the metal (i) is selected from Group VIII of the Periodic Table.

8. A method as claimed in Claim 7 wherein the metal (i) is selected from the group comprising Ni, Pt, Pd, Rh, Ir, and Os.

9. An electrode for a fuel cell whenever produced by the method claimed in any one of Claims 6 to 8.

10. An electrode for a fuel cell comprising a conducting substrate having deposited thereon a catalyst comprising an alloy (as hereinbefore defined) of platinum and rhenium produced by the electrochemical reduction of a solution of hexachloroplatinic acid and a perrhenate.

11. An electrode for a fuel cell comprising a conducting substrate having deposited thereon a catalyst comprising an alloy (as hereinbefore defined) of platinum, rhenium and tin, produced by the electrochemical reduction of a solution of hexachloroplatinic acid, a perrhenate and tin.

12. An electrode for a fuel cell comprising a conducting substrate having deposited thereon a catalyst substantially as hereinbefore described with reference to the Examples.

13. A method for producing an electrode for a fuel cell substantially as hereinbefore described with reference to the Examples.

14. A fuel cell in which an organic material is electrochemically oxidized on an electrode as claimed in any one of claims 1 to 5, 9, 10, 11 and 12.

KILBURN & STRODE,
Chartered Patents Agents,
Agents for the Applicants.

Reference has been directed in pursuance of Section 8 of the Patents Act, 1949, to Specification No. 989,474.

